

LITHIUM ION BATTERIES FOR MARS EXPLORATION MISSIONS

B. V. Ratnakumar, M. C. Smart, C. K. Huang, D. Perrone, S. Surampudi and S. G. Greenbaum*

NASA Jet Propulsion Laboratory, California Institute of Technology,

4800 Oak Grove Dr., Pasadena, CA 91109

*permanent address, Hunter College of CUNY, New York, NY 10021 USA

ABSTRACT

The desired performance characteristics and physical requirements of spacecraft batteries for planetary exploration are reviewed, particularly with respect to surface landers and rovers intended for near-future Mars missions. The use of lithium ion batteries is justified in terms of significant savings on mass and volume, and more importantly of superior low temperature performance deemed essential in the Mars Lander and Rover missions. Use of these batteries in planetary orbiters may require further improvements in their cycle life, especially at shallow depths of discharge. Various strategies currently being adopted to prolong the cycle life for orbiter applications, as well as, for extending their operating range down to temperatures as low as -30°C for more imminent Mars Lander and Rover missions are briefly discussed.

1.0 INTRODUCTION

Planetary exploratory mission spacecraft can be broadly classified into four types: orbiters, landers, rovers, and penetrators. Because of ever-present mass and volume design limitations, batteries intended for use on these exploratory missions have the common requirements of high specific energy and high energy density. With regard to the former, reduction of payload mass dramatically reduces the launch cost, so that the expense of the battery materials is not a critical factor. For example, a 200 kg mass reduction can lead to a \$30 million savings by allowing the use of a lower-cost launch vehicle. Likewise, a compact power source is a necessity, in the context of microspacecraft. In addition to these common features, each of these missions has specific requirements, as listed in Table-1. Briefly, orbiter batteries need to possess extended cycle life, although at relatively shallow depths of discharge. The typical cycle life required is in excess of 30,000 cycles (there is a charge/discharge cycle once each orbit) at 10-30 % depth of discharge (DOD). The battery temperatures of operation are well regulated and are generally above 0°C. On the other hand, batteries in landers and rovers can experience much lower temperatures approaching -30°C. Performance at these low temperatures is thus a key factor for the selection of the battery. The demand on cycle life is, fortunately, not high, with a maximum of 500 deep-discharge (near 100% DOD) cycles being the expectation for both missions. Finally, penetrators require batteries that can operate at even lower temperatures (less than -60°C). Current drains for the penetrator batteries may seem low, but are challenging targets, due to the ultra-low temperatures and the possibility of high shock levels of ~ 80,000 g at time of impacting the hard planetary surface. Currently, lithium - thionyl chloride primary cells are being used in one such Mars Microprobe mission.¹

2.0 RATIONALE FOR LITHIUM ION BATTERIES

Rechargeable batteries based on lithium ion chemistry offer specific energy values 2 to 3 times greater and energy density values 3 to 4 times higher compared to the state-of-art aerospace batteries, i.e., Ni-Cd and Ni-H₂. Combined with its cell voltage (4 V compared to ~ 1.3 for the nickel systems), lithium ion cell exhibits better (coulombic) charge and energy efficiency, due to absence of competing electrolyte reactions (e.g., oxygen evolution). For the reasons of the latter,

the self-discharge rate of lithium ion cell is also low, less than 10% per month. On the other hand, lithium ion cells, unlike nickel systems, have no built-in overcharge mechanism and require appropriate (electronic) charge control. Likewise, sustained over-discharge can impair the reliability of the cell. Nevertheless, these disadvantages are far outweighed by its advantages, such that upcoming planetary exploratory missions are being baselined on lithium ion cells.

Chronologically, rechargeable lithium cells, (i.e., with metallic lithium) have given way to lithium ion cells, (i.e., with lithium intercalating anodes), for reasons of safety and reliability, albeit with a marginal reduction in the specific energy. Lithium ion chemistry is now fairly mature and is being utilized in various civilian applications, mainly portable electronics. For these reasons, lithium ion battery system has been chosen as the prime candidate for the upcoming Mars Exploratory missions. Similar systems with polymer electrolytes, i.e., lithium metal based cells with true polymer electrolytes and lithium ion cells with gel polymer electrolytes, are also being actively pursued and may be viewed as the batteries of the future.

In addition to NASA's Planetary Exploratory missions, other aerospace organizations would also benefit from the advent of aerospace lithium ion cells for a range of applications. Two prominent applications include Geosynchronous Earth Orbit (GEO) and Low-Earth Orbit (LEO) satellites. Recognizing the similarity in the needs of both the organizations, a NASA/DoD Inter-agency effort was initiated with the main intent of developing domestic capability to manufacture lithium ion cells and batteries of desired sizes.² Various key research issues related to the NASA and DoD batteries are being currently addressed. Some of the lithium ion cells (4-40 Ah) being evaluated under this program have fairly impressive performance characteristics, including a specific energy of 100-120 Wh/kg and an energy density of 200-240 Wh/l, and a cycle life of over 500 (to 80% of initial capacity) deep discharge cycles.

3.0 LITHIUM ION BATTERIES FOR NASA APPLICATIONS

Based on the current status of lithium ion rechargeable battery technology, its applicability to various Planetary Exploratory missions will be briefly discussed below.

3.1 MARS ORBITERS

As mentioned above, the cycle life required for the orbiter applications is a few tens of thousands of cycles, though to low depths of discharge, which is a challenging target for lithium ion technology. Only alkaline nickel systems, especially nickel-cadmium and nickel hydrogen (Fig. 1)³ meet this requirement. Generally, for any battery system, the cycle life improves sharply with reduced depth of discharge. However, the extent of this improvement is different for each battery system (Fig. 2).⁴ For example, nickel-metal hydride cells do not display the long cycle lives as observed with Ni-Cd and Ni-H₂ systems, even at low depths of discharge, possibly due to a continued corrosion of the metal hydride anode. Likewise, lithium ion cells also exhibit only a marginal improvement in the cycle life, upon reducing the depth of discharge. Our early results on the Sony 18650 cells with coke anodes reveal that the cycle life improves from about 800 at 100% DOD to only 4000 cycles in accelerated LEO cycling (Fig. 3). Studies carried out elsewhere also confirm that the benefits of low DOD on cycle life is not as prominent in Li ion cells as in Ni-Cd and Ni-H₂.⁵ Most likely, the degradation of the electrolyte, especially towards oxidation at the high oxidation potential during float at 4.1 V, as in LEO cycling, is responsible for such rapid capacity fade rate. In order for Li ion cells to replace nickel systems, therefore, considerable improvements need to be made to the chemistry of lithium ion cells. Various strategies that would be helpful to enhance the cycle life include: a) proper film-forming electrolytes (probably with high EC content), b) moisture-free electrolytes/electrodes, c) carbon anodes with turbostratic disorder (at least on the surface) that would prevent solvent co-intercalation, d) cathodes with no lattice distortion, e) corrosion-resistant cell components and grid materials and f) a proper cell balance that would eliminate lithium plating during charge (during the life of the cell). Use of (true) polymer electrolytes⁶ or solid (ceramic or glassy) electrolytes⁷ might also contribute to extended cycle life.

3.1 MARS LANDERS AND ROVERS

As mentioned in Table 1, one of the critical characteristics for lithium ion cells in Mars Lander and rover applications is the ability of battery to perform reasonably well at low (around -20 to -30°C) temperatures. It is also important that the latter is achieved without much penalty

on the room temperature specific energy, safety, stability or cycle life. It may be realized that non-lithium (aqueous) systems may not be able to satisfy this requirement of low temperature performance without considerably penalty on mass and volume. The research and developmental studies at JPL have, therefore, focussed primarily on this mission-enabling performance characteristic of lithium ion cells.

Although a number of cell parameters have an influence upon the low temperature performance; the electrolyte has been determined to be a key component. One approach to achieving good low temperature conductivity is to use solvents with low viscosity, high dielectric constant, high donor number, low freezing point, and above all with adequate stability towards oxidation (at the cathode) or reduction (at the anode). We have been able to extend the temperature range to lower values, by using selected solvents as ternary or quaternary additives to previously established (filming) electrolyte formulations. For example, a ternary, equi-proportion solvent mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) with LiPF_6 salt and graphite anode provided good low temperature performance, with adequate stability under ambient conditions as well.⁸ Lithium ion cells (D size and larger) containing this electrolyte perform well under the Mars Lander and Rover regimes (Fig.4). Recently, we have examined quaternary electrolyte solutions which include the incorporation of different alkyl esters, and asymmetric alkyl carbonate, e. g., ethyl methyl carbonate, to further improve the low temperature performance (Fig. 5).⁹ From our studies, it is clear that the selection of electrolyte components is crucial to controlling the surface film on graphite anode (termed as Solid Electrolyte Interface, SEI), which not only provides stability but also dictates the kinetics of lithium intercalation-deintercalation.¹⁰

In addition to modifying the electrolyte composition, we have also examined the use of metal oxide anodes, e.g., tin oxides, in place of carbonaceous anodes, to overcome the slow kinetics, if any, across the SEI.¹¹ Another promising approach being pursued is the use of surface modified graphite (with coke-like surface) that would be compatible with propylene carbonate-based electrolytes, instead of EC-based formulations. High capacities of graphite can thus be combined with high interfacial stability of coke. Li ion cells under these conditions will expectedly perform well down to temperatures as low as -40°C .

3.3 POLYMER ELECTROLYTES

The use of polymer or gel electrolytes promises to further enhance the applicability of Li-ion electrochemistry to the space program in two important ways: (1) Polymer electrolytes and electrodes allow for the fabrication of thin, flexible cells which can be fit to many varied form factors, thus allowing batteries to be installed in any available space no matter what the form; (2) Solid electrolytes eliminate the possibility of electrolyte leakage, thus greatly enhancing battery safety. Solvent-free polymer electrolytes offer the greatest possible benefit regarding mechanical integrity, however, they also present the greatest challenge to low temperature operation. For terrestrial ambient temperature applications, a solvent-free polymer electrolyte appears to be a distinct possibility in the near future. The more likely candidate for deployment in the Mars Exploratory missions in the next few years is a gel electrolyte, which is a liquid electrolyte immobilized in a polymeric matrix. A large number of gel compositions have been investigated, with host polymers, such as poly(acrylonitrile) (PAN)^{12,13} and poly(vinylidene difluoride) (PVDF).^{14,15} Recent studies suggest that PVdF gel electrolytes retain fairly high conductivity at temperatures down to -50°C.⁽¹⁶⁾

4.0 CONCLUSIONS

Lithium ion battery technology has shown considerable promise and maturity in portable electronics applications in recent years to warrant a consideration in strategic space applications. Research studies at JPL and elsewhere have culminated in suitable electrolyte formulations that would enable lithium ion cells to function well at sub-zero (Martian) conditions. Efforts are currently underway to utilize this technology in the upcoming Mars Lander application (2001) and Mars Rover missions (2003 sample return). Following these, there will be series of missions (2005 and 2007) to Mars, which will greatly benefit from this technology. For insertion into planetary orbiters, however, further improvements in the cycle life are essential. The use of polymer or solid electrolyte might be helpful in realizing this goal.

5.0 ACKNOWLEDGMENTS

This research was conducted at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration and was supported by the Mars Exploration Program Office. One of the authors (SGG) acknowledges the National Research Council for Fellowship support during his sabbatical leave at the Jet Propulsion Laboratory.

6.0 REFERENCES

1. F. Deligiannis, B. V. Ratnakumar, H. Frank, E. Davies and S. Surampudi, *Proc. 37th Power Sources Conf.*, 373, Cherry Hill, NJ (1996); *NASA Battery Workshop*, Huntsville, AL, Nov. 1997.
2. S. Surampudi et al, *NASA Battery Workshop*, Huntsville, AL, Oct. 1998.
3. Tests carried out for NASA at Crane Div., Nav. Surf. Weapons Center, Crane, IN, 1998.
4. Unpublished data
5. F. Croce, G. B. Appetecchi, L. Persi and B. Scrosati, *Nature*, 394, 456 (1998).
6. B. Wang, J. B. Bates, F. X. Hart, B. C. Sales, R. A. Zuhr and J. D. Robertson, *J. Electrochem. Soc.*, 143, 3203 (1996).
7. M. C. Smart, B.V. Ratnakumar and S. Surampudi, *J. Electrochem. Soc.*, (in press).
8. M. C. Smart, B.V. Ratnakumar, S. Surampudi, and S. G. Greenbaum, ECS Fall Meeting, Boston, MA, Nov. 1998.
9. M. C. Smart, B. V. Ratnakumar, S. Surampudi, Y. Wang, X. Zhang, S. G. Greenbaum, A. Hightower, C. Ahn, and B. Fultz, *J. Electrochem. Soc.*, submitted.
10. M. C. Smart, B. V. Ratnakumar and S. Surampudi, *Proc. 38th Power Sources Conf.*, Cherry Hill, NJ, June 1998.
11. C. K. Huang, J. Sakmoto and S. Surampudi, ECS Fall Meeting, Boston, MA, Nov. 1998.
11. K. M. Abraham and M. Alamgir, *J. Electrochem. Soc.*, 137, 1657 (1990).
12. F. Croce, S. Passerini, and B. Scrosati, *J. Electrochem. Soc.*, 141, 1405 (1994).
13. J.-M. Tarascon, A.S. Gozdz, C.N. Schmutz, F.K. Shokoohi, and P.C. Warren, *Solid State Ionics*, 86-88, 49 (1996).

14. M. Doyle, A.S. Gozdz, C.N. Schmutz, and J.-M. Tarascon, *J. Electrochem. Soc.*, 143, 1890 (1996).
15. P.E. Stallworth, J.J. Fontanella, M.C. Wintersgill, C.D. Scheidler, J. J. Immel, S. G. Greenbaum, and A.S. Gozdz, *Journal of Power Sources*, in press.

FIGURE CAPTIONS

Fig. 1. Typical life cycle curves of A) Ni-Cd and B) Ni-H₂ cells during accelerated LEO cycling.

Fig. 2. Typical variation of cycle life with the depth of discharge in different battery systems.

Fig. 3 Cycle life of lithium ion cells containing coke and graphite anodes in accelerated LEO (40%) test.

Fig. 4. Cycle life of D-size lithium ion cells containing graphite anodes, LiCoO₂ cathodes and 1.0 M LiPF₆/ (1:1:1 EC:DMC:DEC) electrolyte, at 25 and -20°C.

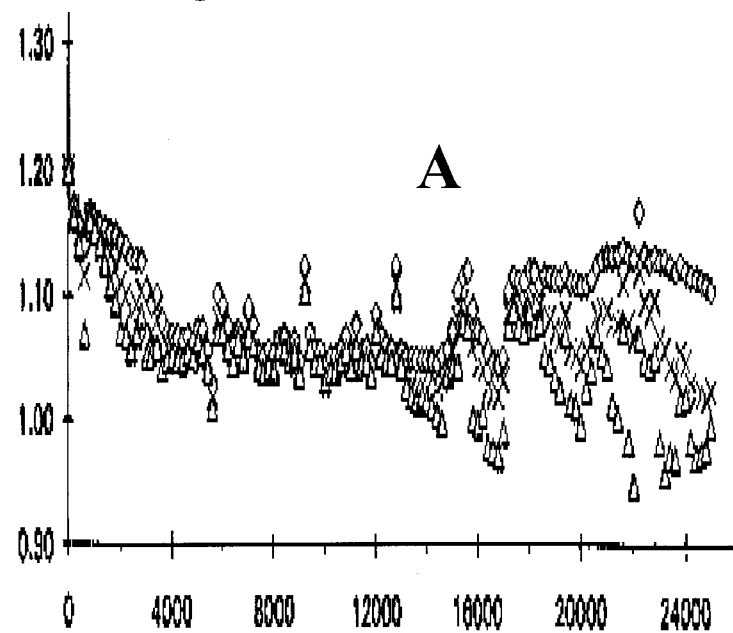
Fig. 5. Electrolyte conductivity measurements quaternary solvent mixtures for lithium ion cells.

Table 1 : Desired performance characteristics of Li ion cells for NASA applications

	LANDERS	ROVERS	GEO	LEO/ PLA. ORBITER	S/C TOOLS	LIBRATION POINT S/C
CAPACITY (Ah)	20-40	5-10	10, 20, 35	10, 20, 35	3-5 AH	20-25 AH
VOLTAGE (V)	28	28	28-100	28	28	28
DIS. RATE	C/5-1C	C/5-C/2	C/2	C/2-C	C/2	C/2
CYCLE LIFE	> 500 (>60%DOD)	>500 (>60% DOD)	2000 (>75% DOD)	>30,000 (>30% DOD)	>100	50
OPER. TEMP, °C	-40 to 40	-40 to 40	-5 to 30	-5 to 0	0-50C	25-30
SP. ENERGY (Wh/Kg)	>100	>100	>100	>100	>100	100
EN. DENSITY (Wh/l)*	120-160	120-160	120-160	120-160	>80	120-160

Fig 1

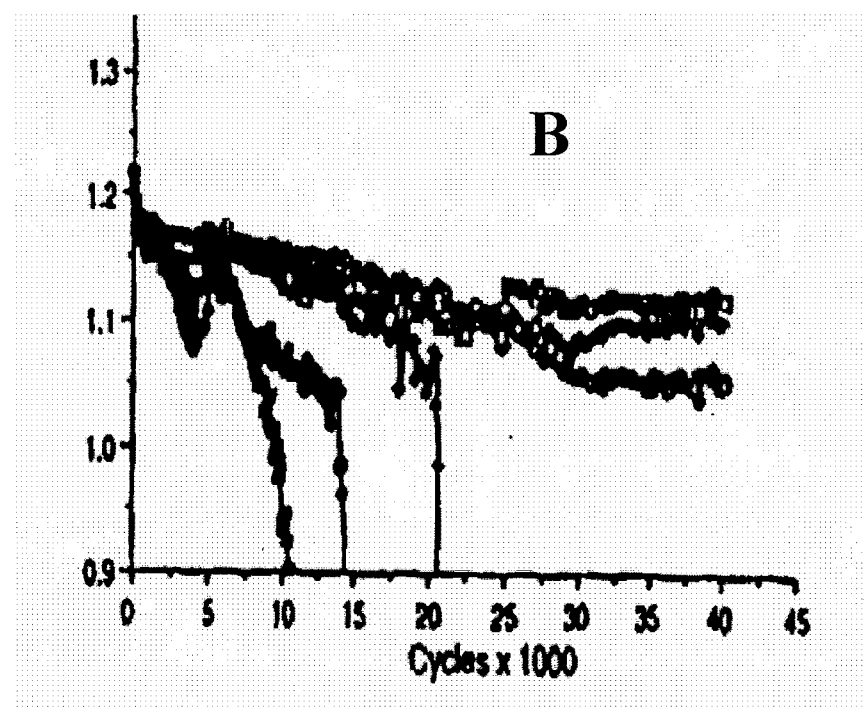
EOD Cell Voltage, V



◇ P1:1 * Rchg

Cycle Number

EOD Cell Voltage, V



Cycle Number

Fig.2

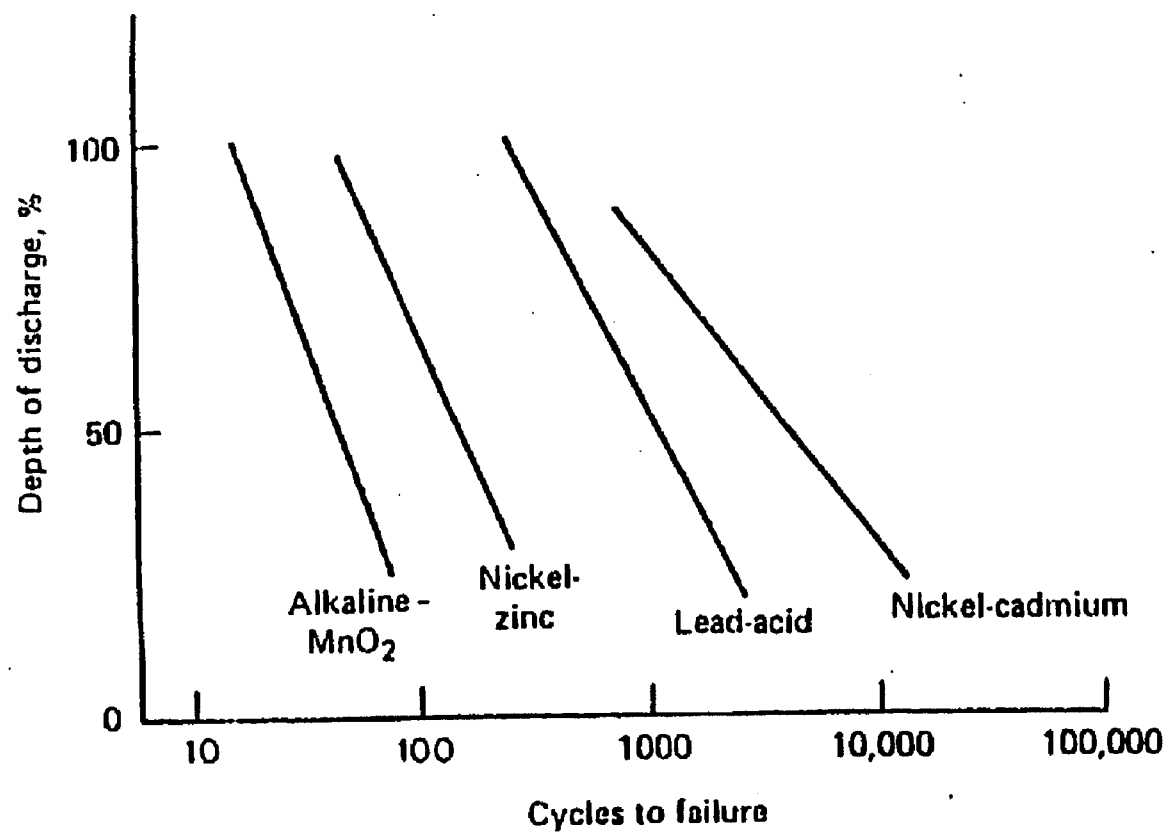


Fig.3

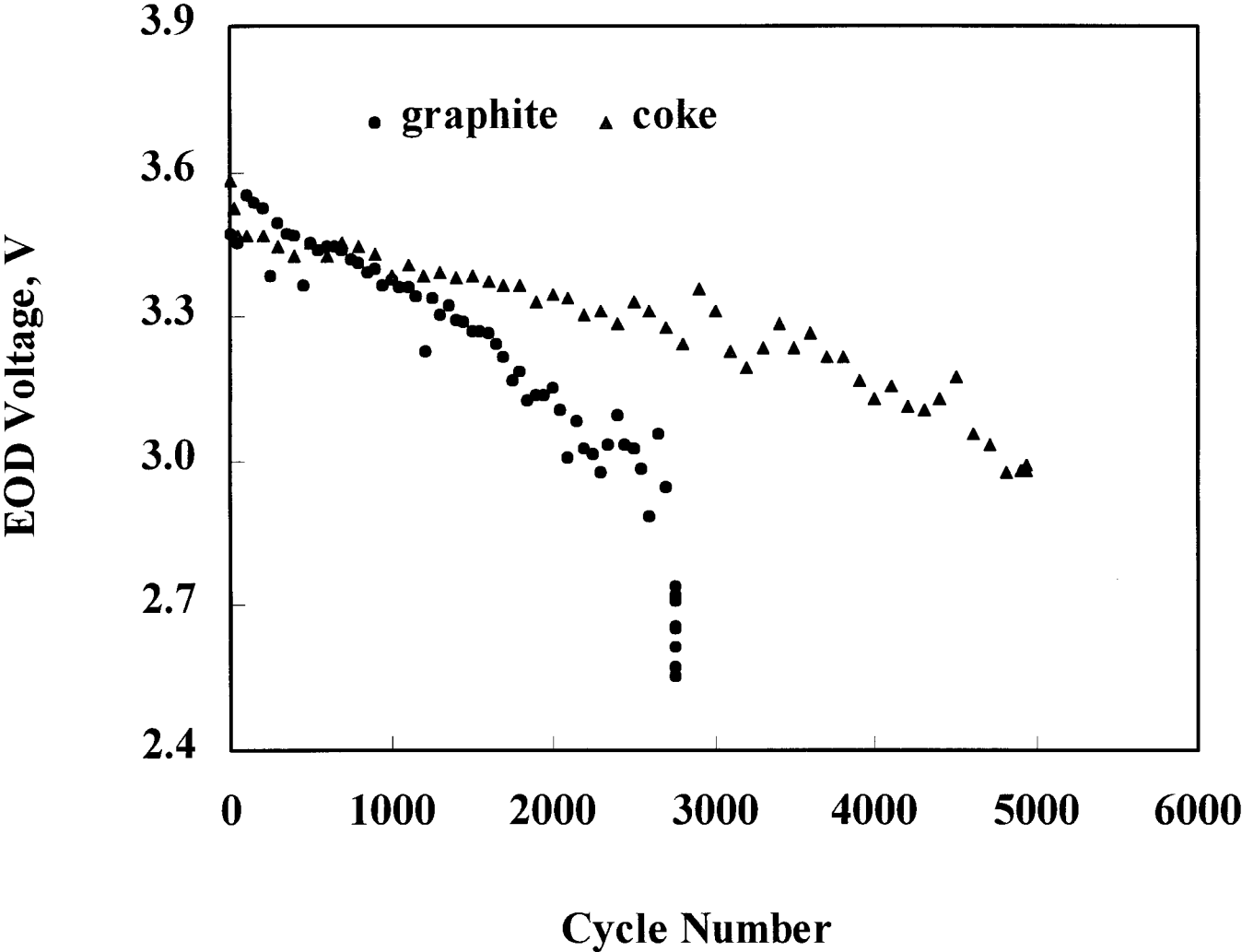


Fig.4

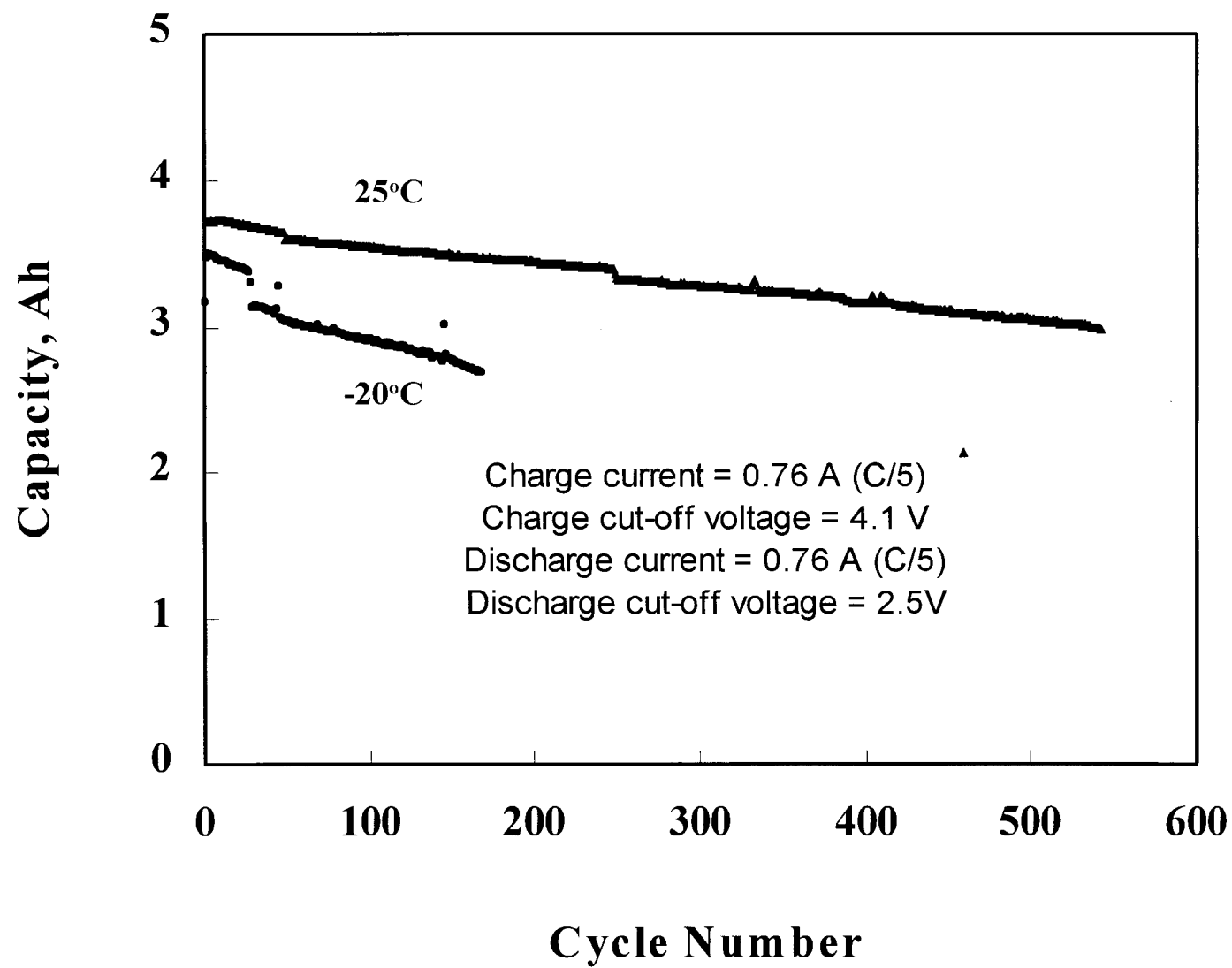


Fig.5

